Wrisley.

Reduction Of Unsaturated Compounds. Fatty Acids And Their Glycerides.

REDUCTION OF UNSATURATED COMPOUNDS. FATTY ACIDS AND THEIR GLYCERIDES

BY

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1 - Introduction.

1 - Introduction.

For many years the problem of converting the unsaturated fatty acids as oleic into the corresponding saturated acid stearic, or the glyceride oleine into stearine, by the simple addition of hydrogen to produce the more valuable hard fats out of relatively cheap raw materials, has occupied much of the attention of the oil chemist.

On the surface the problem would seem simple, because one would expect that hydrogen would add readily at the point of unsaturation. Oleic acid differs from stearic acid in having only a little less hydrogen, for less than one percent of hydrogen is needed to transform oleic acid into stearic acid or oleine into stearine. But this problem has been far from simple, because the unsaturated fatty acids have stubbornly resisted the addition of hydrogen to any marked extent. With the discovery in the last few years of certain hydrogen carriers or catalyzers, it has been possible to carry out the hardening of oils on a commercial scale, and today hydrogenated or hardened oils have become a staple product in the oil market; particularly the hydrogenated edible vegetable oils such as Crisco which is hydrogenated cotten seed oil.

In these commercial processes, the hydrogen gas employed is usually generated by the iron sponge steam process or by the oxy-hydrogen electrolytic cell, and stored in steel cylinders under pressure. Obviously, a more efficient process of reduction or hydrogenation would be to use the hydrogen gas

at the point of generation. With this goal in view, the following study has been made. First, the oils have been suspended in aqueous solution in which the hydrogen gas is being generated by the action of acids on metals. Finally, the electrolytic reduction of fatty acids and their glycerides has been studied where the oil plays the part of a depolarizer in the cells used to generate the hydrogen gas for the catalytic hydrogenation.

11 - Historical.

11 - Historical.

This problem of hydrogenation, with the idea of obtaining a technical process has been attacked in many ways which might be classified as follows:-

1. Hydrogenation by Catalytic Action.
2. Hydrogenation by Ordinary Reducing Agents.
3. Hydrogenation involving the Application of Electricity.

1. Hydrogenation by Catalytic Action.

The very first hydrogenation by catalytic action was reported by Sayzeff[1] in 1871, when he reduced nitrobenzol to aniline by passing the vapors of the former, mingles with hydrogen, over palladium black. But it was not until twenty-five years later that the first real study of metallic catalyzers began with the classical work of Sabatier and Senderens. They laid the foundation for the present processes of hydrogenation of oils. They were the first chemists to recognize the efficiency of nickel and certain other metals as carriers of hydrogen and they carried through a series of experiments,[2] extending over a number of years which demonstrated that unsaturated compounds could be saturated by contact with the gas in the presence of a catalyzer or carrier, such as nickel.

Although much work has been done on the hydrogenation of fatty oils, comparatively little has been published except through the patents, and it is through them that development of hydrogenation must be followed. The first patent record of the

reduction of organic substances by hydrogen is that of J. B. Senderens in 1901. This patent[3] is for the reduction of nitrobenzene to aniline by passing the vapors of the former over heated nickel, copper, cobalt, iron, or palladium in the presence of hydrogen. The hydrogen may be pure or in the form of water gas.

Leprince and Siveke[4] were the first to suggest the possibility of the hydrogenation of oils in a liquid state. From this time on many methods of catalytic reduction have been devised and the patent literature will show some very ingenious apparatus for hydrogenation. A broad study of the various catalysts or hydrogen carriers has been made. A most thorough and interesting review of the catalytic methods of hydrogenation may be found in a book by Ellis, Hydrogenation of Oils, published in 1914.

2. Hydrogenation by Ordinary Reducing Agents.

In 1875, Goldschmidt[5] reduced oleic acid by means of hydriodic acid and amorphous phosphorus at 200° to 210°. This led to the commercial development of a process by de Wilde and Reychler[6] involving the heating of oleic acid to 280° with one percent of iodine, adding and melting with a certain quantity of tallow soap, and then boiled with acidulated water. The product was then distilled and the iodine in part recovered from the pitch. The yield of stearic acid was approximately 70% of the theoretical, and since only about two-thirds of the iodine could be recovered, the process did not find great technical use.

Chlorine has been tried but great difficulty was experienced in securing an autoclave of resistant enough material.

Zurrer[7] chlorinated the fatty acid and then heats with water in the presence of finely divided metal, as zinc or iron. Lewkowitsch alleges that the treatment of monochloro-stearic acid in this manner causes a reversion to oleic acid.

Tissier[8], in 1897, claims a process for the reduction of oleic acid by "nascent"hydrogen. Powdered metallic zinc is placed in an autoclave with water and the fatty material containing oleine introduced and treated under pressure. The glyceride is hydrolyzed to the fatty acid and glycerol, and according to Tissier "nascent" hydrogen is evolved by virtue of the finely divided metal and reduces.the oleic acid to stearic acid. This process is declared to be unsuccessful by Freundlich and Rosauer[9] because such a small amount of reduction is affected.

The action of zinc chloride on oleic acid with a view to converting it into solid material has been tried at a temperature of 200°, without much commercial success although a process by M. V. Schmidt[10] was tried on a large scale in Austrian Candle Works. The quantity of oleic acid that remained unattacked as well as the large amount of liquid unsaponifiable substances formed caused the process to be abandoned.

Lewkowitsch[11] in reviewing the problem states that " "whereas the lower members of the acrylic or oleic series are readily converted into saturated acids, oleic acid itself resists all attempts at hydrogenisation." He carried out a large number of experiments in this direction under most varied con-

ditions, but obtained negative results. The stubborn resistance of oleic acid to the addition of hydrogen is well illustrated by his attempt to hydrogenate in a round about way; that is, by forming the dibromo-addition product and then reducing the latter by hydrogen. He obtained the dibromostearic acid readily, but on attempting to reduce the latter he obtained the original oleic acid.

In 1912, Eric Clemensen[12] published the results of an investigation of the reduction of ketones to the corresponding hydrocarbon with amalgamated zinc and hydrochloric acid. He found that although ordinary reducing agents, such as zinc and acids, sodium amalgam, sodium and absolute alcohols gave either pinacones or secondary alcohols, amalgamated zinc and hydrochloric acid caused the reduction of the ketones to the corresponding hydrocarbons with the greatest ease, and furthermore the yields were excellent, the hydrocarbons pure and no by product was formed. This work would suggest that the hydrogen from the amalgamated zinc must have a greater activity as a reducing agent than ordinary hydrogen and this work furnished the basis for a part of this study of hydrogenation.

3. Hydrogenation Involving the Use of Electricity.

The first one to call attention to the possibility of electrolytic addition of hydrogen to oleic acid was Weineck[13] in 1886. Kuess[14] in 1896 attempted to apply electric current in the steam distillation of fatty acids.

Magnier, Bragnier and Tissier[15] took out patents for

hydrogenation involving the treatment of the fatty material with sulphuric acid, after which the mass is mixed with five to six times its weight of water and then under a pressure of five atmospheres is subjected to the action of an electric current which generates hydrogen in a nascent state. According to Lewkowitsch[16] this process did not amount to much; that is, just as large a yield of stearic acid could be obtained without the electric current.

A process attempting to convert oleic acid into stearic by electrical discharges was patented by A. de Hemptinne.[17] A more detailed account may be found in Ellis, Hydrogenation of Oils, p. 4, (1914).

J. Petersen[18] endeavored to reduce oleic acid to stearic by allowing an electric current to pass between nickel electrodes in an alcoholic oleic acid solution slightly acidulated with sulphuric or hydrochloric acid. The yield of stearic acid was small and at best did not exceed 15-20%. When platinum electrodes were used no reduction at all took place. He also tried to reduce sodium oleate in aqueous or alcoholic solution to the stearate with no satisfactory results.

C. F. Bohringer and Sohne[19] obtained by a similar method much better results when using metallic electrodes as cathodes which were covered with a spongy layer of the same metal. They recommend as cathodes platinized platinum and palladium black. A more detailed account may be found in an article by Lewkowitsch[20] in the J. Soc. Chem. Ind. vol 27, p. 490, (1908).

111 - Theoretical.

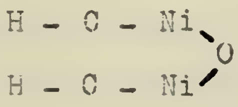
III - Theoretical.

1. Theory of Catalytic Action.

The theory of the action of the catalyst in reduction is one of vital interest in this problem. Much study has been made to determine the exact mechanism of hydrogen addition and the conditions influencing such addition. Catalyzers recognized as useful for this purpose are nickel, platinum, palladium, gold, iron and some others. Nickel oxide has also been employed.

Sabatier[21] considers nickel catalysis to be due to the formation of hydrides. First hydrogen acts on the metal forming a compound in the superficial layer of the latter. The hydride which results becomes decomposed, and in the presence of substances which can take up hydrogen, union with the hydrogen takes place. The metal is regenerated and the role endlessly repeated.

In the case of nickel oxide catalysis, Erdmann[22] indicates that the transference of hydrogen probably takes place in one of two ways; either an intermediate phase represented by the compounds,



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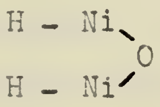


or a decomposition of water may take place in accordance with the reaction,

$$Ni_2O + H_2O = 2NiO + H_2$$

yielding hydrogen in a "nascent" state which is assumed to unite

with the unsaturated fat while the nickel oxide formed is reduced to the suboxide by hydrogen in the molecular condition.

For the exact nature of hydrogen transfer by means of platinum metals the work of Weiland[22] is considered satisfactory. He assumes that palladium hydride, or for that matter, any metal hydride unites as such with the unsaturated compound at the double bond and that the addition product breaks down with retention of the hydrogen and elimination of palladium, the latter being then in condition to take up additional hydrogen and again form an additional product. From a thermodynamic standpoint the hydrogen process appears to be a reversible reaction. Thus the metal addition product would appear in the equilibrium as follows:-

$$-R=R- + PdH_2 \rightleftarrows -\underset{H}{R}-\underset{PdH}{R} \rightleftarrows -\underset{H}{R}-\underset{H}{R} + Pd$$

According to Ellis,[22] Skita and his associates have isolated an addition product of palladium chloride with unsaturated compounds, but work along this line has not been extensive and the explanation advanced that catalyzers simply split the hydrogen molecule to yield hydrogen in an atomic or "nascent" state is as satisfactory as any. A possible explanation of how the metal may cleave the hydrogen molecule into the active atoms or "nascent" state may be seen upon the basis of occlusion. That hydrogen gas is occluded is seen from the following table.

Table 1[23]

Silver wire	0.21
Silver powder	0.91-0.95
Sheet aluminium	1.1-2.7
Reduced cobalt	59 - 153
Copper wire	0.3
Reduced copper	0.6 - 4.8
Iron wire	0.46
Cast iron	0.57-0.8
Reduced iron	9.4 -19.2
Magnesium	1.4
Reduced nickel	17 - 78
Gold leaf	0.48
Precipitated gold	37 - 46
Molten lead	0.11-0.15
Spongy palladium	600 - 700

The numbers indicate the volume of hydrogen under normal conditions absorbed by one volume of the metal. One will note that in this table metals such as Pd, Ni, Co, which are known to catalyze reducing action, there is the marked property of occlusion. The fact that the amount of occlusion as found in the table does not agree entirely with the activity of the metal as a catalyst can be attributed to the physical state of the metal at the time of the measurement, for example gold leaf, which does not act as a catalyzer occludes but 0.48 volume of hydrogen but precipitated gold which does catalyze

reducing action occludes 37 - 46 volumes of hydrogen. The fact remains that the catalytic metals do occlude hydrogen and this must be an essential property of the catalyzer.

2. "Nascent" Hydrogen.

Gaseous hydrogen itself does not exert a reducing action at ordinary temperatures and pressures in most cases, but it was early noticed that the action of dilute acids on metals such as zinc and tin gave hydrogen which would reduce as long as it was in the immediate presence of the metal. This more active state of hydrogen is described as in the "nascent" state. Some theorists have applied the atomic hypothesis to this phenomena and suggest that the greater activity is due to the action of the freshly liberated atomic hydrogen, H, instead of the gaseous molecule, H_2. This would mean that "nascent" hydrogen was a different substance than molecular hydrogen. If this hypothesis of atomic hydrogen is correct, then all methods of giving hydrogen under similar conditions, for example, electrolytic cells with different electrodes and different voltages, would show equal reducing power, but it is a known fact that they do not. Electrodes of different metals do, however, show different efficiencies as reducing agents. This would lead us to believe that the activity of the hydrogen at the point of generation was not entirely due to a different kind or state of the hydrogen. To study such a problem it is necessary to keep in mind all the changes concometant with the reaction producing the hydrogen gas. The effect of each of these concometant changes must be studied

independently. Thus differences in the reducing power may be ascribed to several factors.

It may be due to the other factors of the reactions generating the hydrogen gas which are not usually expressed in the formulas for these reactions. For example,

$$Zn + 2HCl \rightleftarrows ZnCl_2 + H_2$$

is not a complete reaction, for it neglects at least two other manifestations of change; namely, heat and work besides the electrical and other concometants of chemical change. A more complete expression would be,

$$Zn + 2HCl \rightleftarrows ZnCl_2 + H_2 + \text{Work} + \text{Heat}$$

That heat is evolved in this reaction is evident to even the beginner in chemistry. That work is done by the reaction is evident when one recalls that hydrogen gas must escape against the pressure of the atmosphere since $PV = \text{Work}$. If the heat of the reaction generating the hydrogen gas is in part the explanation of the different reducing powers mentioned above, then there should be some correlation between the reducing power and heat of reaction.

In a similar manner, if the work, or more properly the free energy changes of the reaction, is the controlling factor of the reducing power, then some correlation should exist. Since the voltage is a measure of the free energy change, electrolytic reduction offers the best method of showing a possible correlation of this factor, free energy, with the

reducing power. To eliminate any influence of the material of the electrode, a single electrode and electrolyte must be used with varying voltages (i.e. free energy changes). For example, Haber showed that by reducing nitrobenzene at a given electrode with the use of different constant electromotive forces, different products are obtained; that is, different degrees of reduction. The conclusion is, obviously, that the voltage (i.e. the free energy change) is a factor in the electrolytic reduction, and if here, obviously, also in the chemical reduction.

But in this same investigation another factor in the reducing power of hydrogen is shown, for if in the above reduction the voltage and the electrolyte are constant, and the nature of the cathode metal is varied, the velocity of reduction at the surfaces of the different electrodes is different, and would prove a catalytic influence of the nature of the electrode. So with LeBlanc,[24] the conclusion is reached that the catalytic influence of the electrode material, as well as, the voltage plays an important part in the process of reduction.

Just how the nature of the cathode material enters into the problem is receiving much speculation. One interesting line is the work on overvoltage.

On a platinum electrode the reaction,

$$H_2 \rightleftarrows 2H^+ + 2(-)$$

is reversible, i.e., the reaction will go in either direction at the same voltage. Practically no potential difference will be observed between a hydrogen electrode and a piece of platinum

on which the hydrogen is formed electrolytically. However, if a piece of zinc is substituted for the platinum and hydrogen evolved from it, a potential difference as great as 0.7 volts will be observed showing that hydrogen is not evolved reversibly from the zinc. The difference of potential between the metal electrode from which the hydrogen is evolved and a hydrogen electrode in the same electrolyte is called the hydrogen overvoltage of the metal. The following table gives values of the hydrogen overvoltage of some of the metals.

Table 11 (25)

Platinized platinum	-0.00 volts
Silver	-0.15 "
Nickel	-0.137 "
Copper	-0.135 "
Lead	-0.64 "
Zinc	-0.70 "
Mercury	-0.78 "

The cause of these complex overvoltage phenomena has been the subject of much discussion and investigation and even now is not finally settled.

Haber[26] explains it as the adsorption or occlusion of a layer of gas at the electrode; i.e., on the electrode surface, and this film being a poor conductor increasing the potential difference to be overcome by ions passing from electrolyte to electrode, and as its thickness depends on the nature of the

electrode material, the differences observed with different electrodes are explained.

According to Nernst,[27] overvoltage is due to the slow rate at which an electrode, saturated with gas, get into equilibrium with the atmosphere. For bubble formation, a certain minimum gas pressure on the electrode surface is required.

Overvoltage is then an increase in the electrode polarization, due to an increase in the electrolytic solution pressure, caused in turn by the slow rate at which the electrode, charged with gas, gets into equilibrium with the atmosphere.

Later Moller[28] showed that overvoltage and surface tension at the electrode-electrolyte surface runs parallel, and he believes that the cause of the overvoltage is the extra energy necessary to produce, between cathode and electrolyte, a gas film of sufficient thickness to give bubbles.

Overvoltage increases with current density as is shown by the following table giving the overvoltage of mercury at various current densities.

Table 111(29)

Current Density	Overvoltage
0.001 amp/cm^2	1.08
0.01 "	1.12
0.04 "	1.25
0.10 "	1.30

A rise in temperature lowers overvoltage and thereby facilitates hydrogen discharge.

To sum up, the discharge of H ions is followed by the formation of some compound or solution on the electrode surface and the concentration determines potential. This gas concentration itself depends on a number of factors- viz. the rate of decomposition of the same solid solution, current density, time and surface tension relations between the electrode, electrolyte and gas. According to this theory, the energy of reduction depends chiefly upon the height of the cathode potential; that is, the overvoltage, and the best electrodes for reduction would be those at which the overvoltage is highest, namely, mercury, lead and zinc.

The conception of overvoltage is interesting in connection with the dissolving of metals in acid. Pure zinc dissolves very slowly in dilute sulphuric acid. As hydrogen must be evolved from its surface as it dissolves and since the overvoltage is nearly as high as its solution pressure this is to be expected. Amalgamating the zinc decreases its speed of solution as one would expect from the greater overvoltage of mercury which means an increase of the concentration of the hydrogen on the electrode surface, and hence a greater reducing power. The work of Clemmensen,[12] who reduced many ketones to the corresponding hydrocarbons with amalgamated zinc and hydrochloric acid although it could not be done with zinc and hydrochloric acid would tend to show that the hydrogen overvoltage was the essential influence in electrolytic reduction and that there was a possibility that it could be further applied in the reduction of fatty acids and their glycerides.

3. Reduction Involving the Application of Electricity.

Electrolytic reduction may be divided into two classes:[30]

(1) Reductions consisting in an alteration of the charge on an ion such as,

$Fe^{'''} \rightarrow Fe^{''} + \oplus$ and $MnO_4^{'} \longrightarrow MnO_4^{''} + \oplus$

(2) Reduction in which the hydrogen content of the reduced material is increased or its o oxygen content diminished.

$C_6H_5NO_2 + 6H' \longrightarrow C_6H_5NH_2 + 2H_2O \quad 6 \oplus$

In this study of reduction, the second division only applies; namely, the addition of hydrogen to the unsaturated acid or their glycerides. Reductions of this type are considered to consist of two superimposed processes.[30]

(1). Discharge of H ions to atomic hydrogen(or at any rate a form of hydrogen capable of reducing action.

(2) Reduction of the depolarizer by this atomic or active hydrogen.

This depolarization of the H'ion discharge by the material undergoing reduction prevents the hydrogen concentration on the surface of the electrode from reaching the value necessary for the evolution of the gas against atmospheric pressure. Since gaseous molecular hydrogen is known not to reduce under similar conditions of temperature and pressure, any evolution of gaseous hydrogen represents a loss as far as reduction is concerned. Then too, when the depolarization is slow, the concentration of the hydrogen in the electrode, its

solution pressure increases and the cathode potential necessary for the reaction becomes more negative. Not only will the voltage necessary for the reduction be increased, but the current will fall since when the potential needed for hydrogen discharge is reached, a part of the current will produce hydrogen gas. Obviously, the velocity or speed of reduction depends upon the velocity of the second process.

The effect of the cathode material on this reduction may be considered as twofold.[30] Firstly, different cathodes catalyze the reaction between depolarizer and hydrogen at very different rates as shown by the work of Haber and Russ[31] referred to already on page 14. Secondly, an overvoltage action of the cathode can affect electrolytic reduction by increasing the polarization needed for hydrogen ion discharge and according to this overvoltage theory, discussed above, zinc or mercury electrodes should be the best cathode material for the reduction of fatty acids and their glycerides.

Another method[30] involving the use of electricity is that of using as cathode, metallic electrodes which are covered with a spongy layer of the same metal, platinized platinum for example. According to the overvoltage no marked reduction would be expected, but platinum black itself is known to be a powerful catalyzer for reduction. Since the experiments given in this thesis have demonstrated that good results in the way of reduction are obtained with platinized platinum, the explanation must be sought in the occlusive power of the metal rather than any overvoltage phenomena.

lV - Experimental.

IV - Experimental.

Part 1.

Analytical Constants of Hydrogenated Oil.

Analysis and General Discussion of Analytical Constants of Hydrogenated Oils.

The hydrogenation of fatty acids andtheir glycerides causes a marked change in many of their analytical constants, namely, the iodine number, the melting point, but much more characteristic than the melting point is the solidification point for the fatty acids called the titer,[32] the specific gravity, and the index of refraction.

The decrease of the iodine number, by the addition of hydrogen furnishes a ready means of tracing the degree of saturation. The iodine number may be decreases almost to zero by hydrogenation, and on interrupting the process at any stage the original material will have been changed to give products having varied iodine numbers. For purposes of comparison and to give an idea of the nature and degree of the change, the constants for some hydrogenated and unhydrogenated oils will be given.

Table IV.

Kind of Oil	Iodine Number. Unhydrogenated	Hydrogenated.
1. Cottonseed	104 - 116(34)	0 - 10(33)
2. Corn	111 - 124(34)	0 - 10(33)
3. Whale	114	13

The specific gravity and melting point advance hand in hand as saturation increases, the specific gravity approaching that of tristearine, while the melting point in considerable measure depends upon the molecular weight and the hydroxyl content of the fatty acid components of the oil.

Table V.

Kind of Oil	Specific Gravity Original Oil	 Hydrogenated Oil
1. Cottonseed	0.920 - 0.925 (34)	0.9999 (33)

Table Vl.

Kind of Oil	Melting Point[33] Original Oil	 Hydrogenated Oil
1. Cottonseed	Liquid[34]	55.9°
2. Corn	"	55.7°
3. Whale	"	41.5°

The titer test will show a steady increase of the solidification point with increased saturation.

Table Vll.

Kind of Oil	Titer or Solidification Point Original Oil	 Hydrogenated Oil
1. Cottonseed	32°-35°	32°-38°
2. Corn	19°	
3. Whale	23.9°	45°

The index of refraction is also greatly modified.

Index of Refraction at 55°(33)

Abbe Refractometer.

Table VIII

Kind of Oil	Original Oil	Hydrogenated Oil
1. Cottonseed	1.4588	1.4496
2. Corn	1.4615	1.4514
3. Whale	1.4603	1.4550

In this study we have limited ourselves to the iodine number and solidification point or titer, for tracing the progress of hydrogenation.

The iodine number has been determined according to the method of Hanus[35]. The iodine number is the percentage of iodine (or of iodine bromide, in this method, expressed in terms of iodine) absorbed by the sample. This number gives a quantitative measure of the unsaturated fatty acids in the sample.

Hanus Method.

This is the method used universally in America and is the one adopted by the Association of Official Agricultural Chemists. Hanus used a solution of iodine monobromide in glacial acetic acid (99.5%), prepared as follows:- 13.2 grams of iodine are dissolved in one liter of glacial acetic acid(99.5%) adding enough bromine to double the halogen content, determined by titration with thiosulphate. The thiosulphate solution should be approximately tenth normal, and the potassium iodide 150 grams per liter. The solvents used are chloroform or carbon-

tetrachloride which are treated for purity by adding a known amount of the iodine solution and then titrating back and etc. The starch solution for an indicator should be made fresh for each determination by stirring 0.5 gram of starch in 50 cc of cold water, and then boiling it gently. The

The method is essentially as follows:-

1. Standardization of Sodium Thiosulphate Solution.

Exactly 3.8694 grams of pure dry potassium dichromate, were dissolved in water and diluted to 1000 cc. In a well filled tightly stoppered bottle this standard solution will keep indefinitely without deterioration. Each cubic centimeter of this solution is equivalent to 0.01 gram of iodine. 25 cc of a 15% potassium iodine solution are mixed with 5 cc of hydrochloric acid, and 50 cc of the dichromate solution are added and the liberated iodine titrated by means of the thiosulphate solution using the usual procedure and precautions.

The amount of iodine consumed by each cubic centimeter of the thiosulphate solution is then calculated.

2. Determination:- Into a thoroughly dry and clean Erlenmeyer flasks fitted with accurately ground stoppers is weighed from 0.10 - 0.20 gram of the oil. The oil is then dissolved in 10 cc of chloroform. After complete solution has taken place, 25 cc of the iodine solution are added. The mixture is allowed to stand, with occasional shaking, for thirty minutes. The excess of iodine should be at least 60% of the amount added.

3. Titration of the unabsorbed Iodine:- Ten cc of the potas-

sium iodide solution is added, with 100 cc of distilled water. The excess of iodine is titrated with the sodium thiosulphate solution using the starch solution as an indicator and observing the usual procedure.

Each time that the iodine solution is used, its value must be determined by running two "blanks" and carrying them through with exactly the same manipulation as in the determination of the fat.

4. In explanation of my method of calculation an example is now given.

Iodine Value.

			Blank	
	1	11	1	11
Weight of tube plus sample	20.9755	20.7793	-	-
Weight " " "	20.7793	20.5614	-	-
" " "	0.1962	0.2179		
Cc of chloroform	10	10	10	10
Cc of Hanus Solution	25	25	25	25
Cc of Thiosulphate	40.6	38.5	57.2	57.4
Cc of Thiosulphate*	16.7	18.6	-	-
Iodine Number	106.2	107.0		

* Thiosulphate equivalent to the iodine absorbed. 1 cc of the $Na_2S_2O_3$ is equivalent to 0.0125 gram of iodine.

Explanation:- The number of cc of the thiosulphate solution equivalent to the "blank" of 25 cc of Hanus iodine solution minus the number of cc of $Na_2S_2O_3$ needed to titrate the excess of Hanus solution represents the thiosulphate equivalent of the iodine absorbed. Since the iodine number equals the percentage of iodine absorbed by the fat expressed in terms of iodine, a numerical illustration would be as follows:-

$$\text{Iodine number} = \frac{16.7 \times 0.0125}{0.1962} \times 100 = 106.2$$

Titer Test:-[32] The fat under examination is saponified and the separated fatty acids are freed from water and finally filtered through a dry plaited filter into a small porcelain dish. The fatty acids are allowed to solidify and stand over night under a desiccator. The fatty substance is carefully melted, and poured into a test-tube, 16 cm long and 35 cm wide till the test-tube is a little more than half full. The tube is then fastened by means of a cork into a wide mouth bottle, and an accurate thermometer is inserted in the fatty acid, so that the bulb is in the center of the mass. The tube will gradually cool and when a few crystals appear at the bottom of the tube the mass is stirred with a quick circular movement by the thermometer, until the mass has become cloudy throughout. The thermometer should then be carefully observed. At first the mercury will continue to fall, at least remain stationary, then it will rise suddenly some tenths of a degree and reach a maximum, remaining stationary a little time before it falls again. This point is called the"titer" or solidifying point of the mixed fatty acids.

IV - Experimental.

Part II

IV - Experimental.

Part II.

Catalytic Reduction.

In order to understand and appreciate the classical work of Sabatier and Senderens on catalytic reduction, it seemed best to set up the necessary apparatus, prepare the catalyzer, and actually carry out this process of reduction in the laboratory. For a guide, experiment 11, entitled "Reduction of Hydrocarbon, Benzene in the presence of Finely Divided Nickel," Sabatier's Method, in Laboratory Manual of Organic Chemistry by Dr. W. A. Noyes, was used.

It seemed that the Volhard bath, which was to be filled with high boiling gasoline or kerosene which is set to maintain a temperature of 195° by distilling away the low boiling portion till that temperature was reached in the bath, would be very cumbersome and difficult to regulate and control, especially when working with hydrogen gas. It was decided to build an electric furnace to be used for the tube to be filled with nickel over which the vapors would pass.

Construction of the Electrically Controlled Carius Furnace[36].

The core of the furnace consisted of an ordinary gas pipe three inches in diameter and thirty inches long. This pipe was threaded on both ends, and fitted with heavy iron screw caps making the total length thirty-two inches. A five-eighth inch hole was placed in the end, and near the edge of one of the caps through which the pyrometer couple might be introduced into the

furnace, and also to act as an outlet for gas incase of an explosion.

A strip of asbestos paper 28 inches wide and of sufficient length to make a wrapping of three thicknesses was moistened and wrapped tightly around the pipe in such a way as to leave the threaded ends of the pipe uncovered.

A loop of No., 18 copper wire was fastened tightly around one end of the pipe over the asbestos, allowing a sufficient lead from the loop to make connections(external connections). Thirteen feet of No. 30 nichrome wire(diameter 1.252 mm) was wound uniformly around the asbestos covered pipe, and fastened firmly to the copper loop at each end. This coil was then covered with three layers of moistened asbestos paper, and a second coil of nichrome wire with copper terminals wound around over it. This process was repeated a second time making a total of three coils on the furnace. The last coil was covered with moistened asbestos until the diameter of the pipe plus the asbestos covering was five inches thick, and the whole allowed to dry. A portion of "magnesia mixture" steam pipe was fastened around this core in such a way as to allow the threaded ends plus the pipe to project and be of easy access. In order to prevent loss due to heat radiation at the end, caps of "magnesia mixture" were made. Each cap consisted of a section of the "magnesia mixture" four inches long, lined with sheet aluminium three inches in width.

2-Calibration of the Furnace.

For the calibration of the furnace a Hoskin pyrometer was

used to measure the heat and an alternating current voltmeter and ammeter were used to measure the electircal power consumption. A section of ordinary combustion tubing the length of the furnace was placed within it, and in line with the holes in the iron and magnesium caps, so that when the pyrometer thermo-couple was pushed through the cap holes it went inside of the glass tube. The coils were numbered one, two, and three respectively, numbering from the inner out and the following calibration made.

Coil Number One.

The end of the thermo-couple was placed at the center of the furnace with the following results.

Time				
Hours	Minutes	Temperature	Amperes	Volts
0	0	25°	1.3	115
0	15	30°	1.3	115
0	50	80°	1.35	116
1	03	87°	1.35	116
1	20	105°	1.3	115
1	55	125°	1.3	115
2	25	145°	1.2	112
2	50	160°	1.2	112
4	03	180°	1.2	112
5	04	190°	1.1	110
6	10	200°	1.1	110
7	15	215°	1.0	109

The end of the thermo-couple was placed two thirds of the way into the furnace. The temperature rose to 222° as a maximum.

The thermo-couple was then placed one-third of the way into the furnace and the temperature fell back to 210°. Hence the variation in the temperature within the furnace was about 12° for heating coil No.1

Coils One and Two Combined.

The end of the thermo-couple was placed at the center of the furnace with the following results:-

Time				
Hours	Minutes	Temperature	Amperes	Volts
0	0	25°	2.5	109
0	16	50°	2.5	109
0	25	75°	2.4	108
0	45	100°	2.2	105
0	53	120°	2.2	105
1	05	140°	2.3	107
1	10	160°	2.4	108
1	30	180°	2.1	101
1	50	200°	2.1	101
2	18	220°	2.0	99
2	38	240°	2.0	99
2	57	260°	2.2	105
3	13	280°	2.2	105
3	30	300°	2.4	108
3	51	320°	2.4	108
4	15	340°	2.3	107
5	00	340°	2.3	107

The end of the thermo-couple was then placed two-thirds of the way into the furnace. The temperature rose to 345° as a maximum, but when the thermo-couple was placed one-third of the way into the furnace the temperature fell to 338°. As above, the temperature within the furnace was constant within 10°.

Coils One, Two, and Three Combined.

The end of the thermo-couple was placed at the center of the furnace with the following results:-

Time Hours	Minutes	Temperature	Amperes	Volts
0	0	18°	3.85	102
0	10	35°	3.8	102
0	25	90°	3.75	102
0	35	125°	3.70	101
0	50	175°	3.70	100
1	00	190°	3.70	100
1	09	208°	3.65	100
1	30	250°	3.65	100
1	45	270°	3.65	100
2	00	295°	3.65	100
2	42	345°	3.65	100
3	22	375°	3.65	100
3	50	390°	3.60	98
4	48	415°	3.60	98
5	48	435°	3.60	100
7	30	460°	3.60	98
8	45	462°	3.60	100

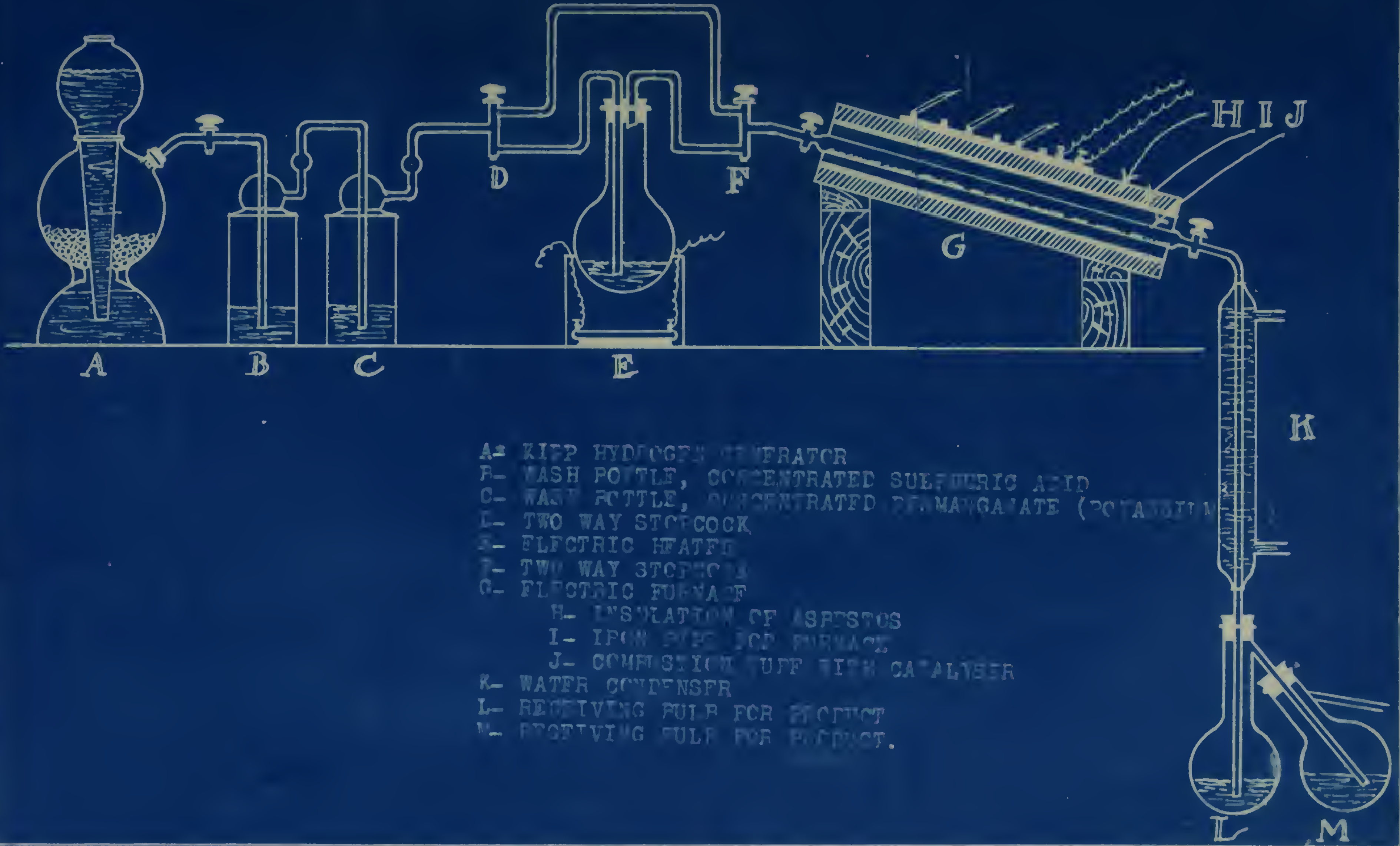
With the thermo-couple placed two thirds of the way into the furnace the temperature rose to 465° as a maximum, but when placed one third of the way in, fell to 455°.

This furnace was made easily and at a low cost of time and materials. As the experiments will show, it proved to be an efficient electric furnace. The cost for electricity, when a maximum capacity of three coils is used is only about three cents per hour calculated at the rate of ten cents per kilowatt hour. In practice, the temperature desired was more quickly reached by using all three coils combined, and maintained with the aid of resistance or by alternately switching on and off one or more of the coils.

3. Preparation of the Catalyzer.

Twenty grams of metallic nickel were almost completely dissolved in 500 cc of dilute $HNO_3(1{:}3H_2O)$. This solution was poured off, leaving behind some undissolved nickel, into a porcelain dish which contained some powdered amorphous silica and the mixture thoroughly stirred. It was allowed to evaporate, with frequent stirring, to almost a claylike, solid consistency. This was then crushed to small pieces, and heated in a nickel crucible. At first the mixture became almost liquid, due to water of crystallization, then sticky and finally crusty again. Then the red fumes of nitric oxide began to come off. With stirring and continued heating the rather course lumps turned from a green color to a brown to a greyish black, and after some time the fumes ceased to come off and I concluded that I had nickel

FIGURE 1



A= KIPP HYDROGEN GENERATOR
B– WASH BOTTLE, CONCENTRATED SULPHURIC ACID
C– WASH BOTTLE, CONCENTRATED PERMANGANATE (POTASSIUM
D– TWO WAY STOPCOCK
E– ELECTRIC HEATER
F– TWO WAY STOPCOCK
G– ELECTRIC FURNACE
H– INSULATION OF ASBESTOS
I– IRON PIPE FOR FURNACE
J– COMBUSTION TUBE WITH CATALYSER
K– WATER CONDENSER
L– RECEIVING BULB FOR PRODUCT
M– RECEIVING BULB FOR PRODUCT.

oxide mixed intimately with the silica as a carrier.

Experiment 1.

The apparatus was set up as described in the figure on the opposite page, Figure 1, so that the hydrogen from the Kipp generator passes first through a concentrated solution of potassium permanganate, then through concentrated sulphuric acid then through a distilling bulb containing 50 grams of benzene (boiling point 80°-82°). The latter was placed over an electric heater. The combustion tube containing the catalytic material is placed in the electric furnace and the lower end connected to the neck of a 200 cc distilling bulb surrounded with ice water. The side tube of this bottle is connected to a tube dipping into 25 cc of alcohol contained in a second distilling bulb, which is also surrounded with ice water. The alcohol is to retain vapors of cyclohexane which escape condensation in the first bulb.

After starting the passage of hydrogen through the system it was tested for leaks by closing the stop-cock at the end of the apparatus. As soon as this cock was closed the flow of hydrogen ceased and the acid rose in the Kipp generator showing no leaks in the system. The electric furnace was started at this time.

Although there was a vigorous evolution of hydrogen into the system, it was absorbed before it reached the distilling bulb at the end of the system, since no bubbles could be detected. This hydrogen was passed through the upper path and not through the benzene, because the catalyzer must be reduced with hydrogen

before it becomes active. After about one hour, the temperature of the furnace, determined by a pyrometer, was 200° and about this time water vapor was noticeable at the end of the combustion tubing showing that the nickel oxide was being reduced. The temperature in the electric furnace continued to rise till in one and three-quarters hours the temperature reached 295°. Hydrogen had been passing through all this time, and the water vapor finally ceased to come over from the tube. According to Sabatier, the catalyzer is most effective after being freshly reduced at a temperature of 220° to 300°, and the reduction most effective at a lower temperature 190° to 200°, the current to the furnace was turned off, and the furnace allowed to cool while a steady flow of hydrogen gas was maintained. After about two and a quarter hours the temperature of the furnace was 190°.

Then the two way stopcock was set so that the hydrogen gas passed through the bulb containing the benzene. To insure the proper excess of hydrogen with benzene vapors, the temperature should be kept about 35°. However, the temperature control at this point was very poor due to the lack of control of the electric heater and the temperature varied from 35° to 60°. Throughout the experiment, the benzene vapors condensed in the tubes running to the furnace and it was necessary to warm them in order to force the benzene vapors through into the catalyzing tube. A little liquid collected in the first flask(L). The temperature of the furnace was maintained at 190° to 200° for four hours by throwing in or out of the circuit one or more of the heating coils, while a steady stream of hydrogen was passed

into the system. While the tube was cooling a stream of hydrogen gas was passed through it. After cooling, the catalyzer was sealed in an atmosphere of hydrogen by closing the two ends of the tube securely with stopcocks.

Weight of the benzene in the bulb at the start.... 50 gms
" " " " " " " " " end ...... 25.8 "
" " " " treated 24.2 "

On removing the combustion tube from the furnace, it was noticed that the catalyzer had changed from a grayish black to an almost coal black substance, showing reduction of the nickel oxide to metallic nickel.

A very small amount of the product was thrown out of the alcohol solution of it in the bulb (M) upon dilution with water. After separating, it was added to the product in the flask (L). This was dried and weighed 21.5 grams showing that 89% of the initial material could be accounted for. This material had a marked gasoline odor. The product did no decolorize $KMnO_4$ aq., showing that hexenes were absent. The benzene was separated from the cyclohexane by shaking with an equal volume of fuming sulphuric acid in a flask attached to a reflux condenser to prevent loss by volatilization. With this treatment any benzene present would be converted into benzene sulphonic acid, soluble in water; whereas, the cyclohexane would not be attacked. Little heat was generated. After shaking for one half hour there was still a good amount of substance insoluble in the fuming sulphuric acid, and the mixture was separated. The upper layer containing the product, cyclohexane, was washed with four volumes of cold water.

A clear layer of liquid separated out above the water. A slight odor of SO_2 along with a distinct odor of gasoline was detected. This upper layer after separating was dried over $CaCl_2$ and weighed 13.9 grams. Although some of the substance was no doubt lost by volatilization during the manipulation, there must have been considerable benzene which passed over unhydrogenated. Actual yield of cyclohexane was 13.9 grams equivalent to 64.6% of the total material which was obtained at the end of the reduction. This product was fractionally distilled from a water-bath. The temperature rose rapidly to 79.5° and then slowly to 81°.

	Weight
1st fraction 79.5° to 80°......... ...	7.8 grams
2nd fraction 80° to 81°	5.3 "

A residue of one-half cubic centimeter remained. Cyclohexane boils at 81°. Benzene boils at 80.12°. The product obtained boils at 79.5°-81° uncorrected.

Temperature read	79.5°-81°
Stem exposure	80°-81°
Average stem exposure	50°
Room temperature	25°
Barometeric pressure	746 mm

which corresponds to 79.9°-81.4° corrected.

In order to test the cyclohexane for benzene, a few drops in a test tube were warmed with a mixture of 3 cc of concentrated sulphuric acid and 3 cc of nitric acid (sp.gr. 1.42). The reaction mixture was distilled with water and extracted with hydrochloric acid and tin. After warming a short time an excess

of NaOH(1:10) was added, and the whole extracted with ether. The residue was tested for aniline by dissolving it in water and adding a filtered solution of chloride of lime when, if aniline had been present a transient purple color would have been observed, but such was not the case proving the absence of aniline and hence benzene from the original product.

Mr. S.D.Kirkpatrick who was studying the solubility reactions of dimethyl sulphate used some of my hydrogenated benzene or cyclohexane. Aromatic hydrocarbons are soluble in dimethyl sulphate and aliphatic saturated hydrocarbons are insoluble in it. He found that my product was totally insoluble in dimethyl sulphate showing conclusively that my product was a saturated aliphatic hydrocarbon, cyclohexane.

General Summary and Conclusion.

The electric furnace built for this experiment proved to be efficient, and the temperature was readily controlled. The small heater built for vaporizing the benzene was efficient as a heater, but the temperature control was poor, and with better regulation a higher yield of cyclohexane would have been obtained. The fact that in the first experiment, the catalyzer was active shows that it must be an efficient catalyzer and that by studying the conditions more closely and with experience it would be a very effective agent for catalyzing the hydrogenation of fats and oils.

However, this study was started with the view of utilizing the hydrogen at the point of generation, so this finished the experimental study with nickel as a catalyst.

Part 111

Hydrogenation by Ordinary Reducing Agents.

Hydrogenation by Ordinary Reducing Agents.

Experiment 1. **Part 111.**

With the work of Clemmensen in mind, an attempt to reduce or hydrogenate cottonseed oil was made. Two hundred grams of granulated(mossy) zinc was allowed to remain in 400 cc of a 5% mercuric chloride solution for one hour. The zinc took on a grayish coating showing that the zinc was being amalgamated. The liquid was then poured off, leaving the treated zinc behind in one liter round bottom flask. A reflux condenser was connected to the flask, and 25 grams of cottonseed oil and 50 cc of HCl (one part acid to two parts water) was added. A vigorous evolution of hydrogen gas followed which gradually slowed up. The cottonseed oil floated upon the surface and in order to produce a brisk evolution of hydrogen, and to secure a thorough mixing of the three constituents, zinc, acid and cottonseed oil a gas burner was started under the flask. With continued boiling the oily layer disappeared due to the oil adhering to the zinc. After boiling the mixture for two hours and a half, the burner was turned off, and the mixture left over night. The next morning 50 cc of HCl (1:2H_2O) was added, and the heating continued. This time, and from then on, commercial HCl,(one part crude acid to two parts water) was used, because there are certain impurities in it such as iron which serve to accelerate the action of the acid on the zinc. After boiling for seven hours, making a total of nine and a half hours, the heat was shut off and the flask cooled. The mixture was poured into a separatory flask, and extracted twice with petroleum ether.

The separated ether was filtered, dried over anhydrous sodium sulphate, filtered again, and the petroleum ether distilled off. The treated oil was slightly darker than the original cottonseed oil, and was a little more viscuous. A slight odor of petroleum ether was still noticeable, so the oil was dried over night in an air bath at 100°. The next morning some white crystals separated out which were filtered off and dried by means of a filter pump. The cottonseed oil was liquid at 26.5° and solid at 26.2°. The white crystals melted at 69° uncorrected which was 69.4° corrected.

Average temperature of stem	40°
Stem exposure..................	71°
Room temperature	24°
Barometer	744 mm

The iodine numbers of the original and treated cottonseed oil were obtained with the following results.

Table 1X

Sample		Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$*	Iodine Number
Blank		-	-	62.05	-	-
Blank		-	-	61.95	-	-
Original	Cottonseed oil	0.0	0.1520	47.0	15.0	109.0
"	"	0.0	0.2390	38.45	23.55	108.3
Treated	"	9.5	0.2005	42.35	19.65	105.0
Treated	"	9.5	0.1785	45.25	16.75	103.5

* $Na_2S_2O_3$ equivalent to the iodine absorbed. 1cc of $Na_2S_2O_3$ is equivalent to 0.0110 gram of iodine.

These results would show that some reduction had taken place, but it is apparently very slow, and if it is to be a successful method of reducing cottonseed oil, it must be made to go faster. The crystals which separated out of the treated cottonseed oil, melting point, 69°, can be explained only by assuming that some of the cottonseed oil was hydrolyzed to the fatty acid which was reduced to stearic acid. In opposition to this view is the fact that with NaOH using phenolphthalein as an indicator, .02 g required only 1/10 cc of the alkali for neutralization. This would seem to indicate that the solid was stearine in an impure form. Repeated experiments failed to yield this product again.

Experiment 11.

Believing that a more intimate mixture of the amalgamated zinc, acid and cottonseed oil would hasten the reduction, the first experiment was repeated using 200 grams of amalgamated zinc dust instead of the amalgamated granulated zinc. Thirty grams of cottonseed oil and 50 cc of concentrated HCl (1:2H_2O) with the amalgamated zinc dust was heated up in a flask with a reflux condenser as before. The oil was intimately mixed with the zinc dust, and at no time was a distint layer of the cottonseed oil visible on the upper surface of the mixture. After four hours another 50 cc of concentrated HCl(1:2) was added. The cottonseed oil seemed to cause the zinc dust to cake and only the vigorous boiling and hydrogen gas evolution kept the two from forming an almost solid mixture. The heating was continued for twelve hours, after which the flask was cooled and the treated oil obtained by

extraction with petroleum ether and purified in the usual way. This treated oil was noticeably darker and slightly more viscous than the original cottonseed oil, but no white crystals separated out as in the previous experiment. Much to our surprise, the iodine numbers of the original and treated cottonseed oil were alike, showing that no reduction had been effected. In order to determine whether the cottonseed oil had been saponified to any extent, one gram of it was titrated with 0.0822N KOH and it required 7.4 cc for neutralization which would mean 17.1 percent of free fatty acid in the cottonseed oil.

It would seem that if the amalgamated zinc and acid were going to be serviceable as an effective reducing agent that at least a trace of reduction would have taken place even if the correct conditions for the best reduction were not present. However, it was deemed advisable to continue studying this method with the idea of finding the conditions with which this reduction would take place. With only slight variations, this same method was tried out in eight separate experiments with the following results.

Experiment 111.

Instead of using 200 grams of zinc dust, at one time at the beginning, and adding 50 cc of concentrated HCl (1:2H_2O) each time, 20 grams of zinc dust were treated or amalgamated at the same time and 20 grams added every two hours until 200 grams was added. Also, aside from the first addition of 50 cc of the acid, twenty cc were added at intervals of one hour throughout the time of the experiment. The heating was continued 44 hours which was

a much longer time than in the previous experiments. The treated cottonseed oil was quite viscous , but of a decidedly dark brown color. Evidently prolonged heating darkens the oil. The greater viscosity of the treated oil was at first thought to be a sign of hardening or reduction, but the iodine numbers of the original and treated oil were the same, which again proved that no reduction had been effected. One gram of the treated oil required 16 cc of 0.0822 N KOH for neutralization, which is equivalent to 37.1% of free fatty acid in the oil. The presence of fatty acids would explain the greater viscosity of the treated oil, because the solidification point of the fatty acid is much higher than that of the ester.

Experiment lV.

The last experiment was repeated in detail with the one exception that iron filings were substituted for zinc dust. A much darker colored product was obtained which showed no trace of reduction according to the iodine numbers.

Experiment V.

This was a repetition of experiment lll with the exception that the concentrated HCl(1:2H_2O) was replaced by the concentrated crude acid which caused a more brisk evolution of hydrogen at all times, and the treated product was of a much darker color and more viscous than the treated cottonseed oil in experiment lll. One gram required 20 cc of 0.0822 N KOH for neutralization which is equivalent to 46.3% of free fatty acid. This would demonstrate that the stronger the acid and more brisk evolution of hydrogen

favored saponification and hence the greater viscosity of the product.

Experiment Vl.

According to Clemmensen a vigorous evolution of hydrogen is necessary so with that in mind the conditions of experiment ll were duplicated, and in addition a few crystals of copper sulphate were added from time to time which caused a tremenduous increase in the evolution of hydrogen gas. The cottonseed oil obtained was darker than that obtained in experiment ll and was far more viscous in fact almost a solid at room temperature. This would suggest that the increased evolution of hydrogen due to the addition of the copper sulphate favored hydrolysis and this was confirmed since 1.2 gram of the treated oil required 34 cc of 0.0822 N KOH which is equivalent to 65.6% of free fatty acid. Again the iodine number of the treated oil evidenced no reduction.

Experiment Vll.

The third experiment was repeated as described with one exception; namely, crystals of copper sulphate were added to accelerate the evolution of hydrogen gas. For ten hours a most vigorous evolution of hydrogen was maintained and the zinc, acid and cottonseed oil seemed to be thoroughly mixed at all times. The treated oil was darker in color than the product of experiment lll, but more viscous, being almost solid at room temperature. A gram sample required 26.5 cc of 0.0822 N KOH which is equivalent to 61.4% of free fatty acid in the treated cottonseed oil. As in the previous experiments the iodine number showed no trace of reduction.

but considerable hydrolysis of the cottonseed oil.

Experiment V111.

It is essential that a thorough mixing of the three constituents be obtained. So far, this has been accomplished by heating whereby the brisk evolution of the hydrogen and the mechanical effect of boiling keeps the mixture thoroughly agitated and mixed. However, the heat and increased evolution of hydrogen seem to favor hydrolysis which may in some way prevent reduction. In order to obtain a thorough mixing and at the same time avoid superheating and a too vigorous evolution of hydrogen a double walled round bottom flask was used. Live steam was run into the outer jacket to heat up the mixture and also live steam run into the flask which kept the contents well mixed. As in experiment 3 the zinc was amalgamated and added from time to time as was the concentrated $HCl(1:2H_2O)$. After the process had continued six hours, the flask was accidentally cracked and the experiment was discontinued. A sample of the treated oil was almost as light colored as the original oil and of the same consistency. However, the iodine number, as before, showed no change or no reduction with little saponification.

Experiment 1X.

Another double walled flask was obtained and the last experiment repeated except that the process was continued for fifteen hours after which a sample of the treated oil was taken. This too was of almost the sample color and consistency as the original cottonseed oil. One gram of the treated oil required 2.3 cc of

0.0822 N KOH which is equivalent to 5.33% of the free fatty acid in the sample, and again the iodine number of the treated oil was the same as the original.

Experiment X.

One more effort was made to obtain reduction by means of amalgamated zinc and hydrochloric acid. Experiment 1 was repeated in detail, and the process was continued for 15 hours but again the treated oil showed no reduction as proved by the iodine numbers.

General Summary and Conclusions.

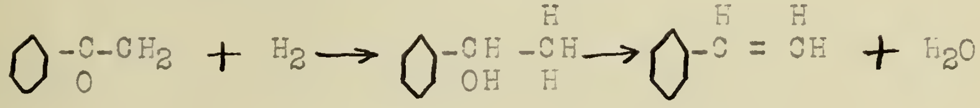
These attempts to reduce cottonseed oil or its fatty acid with amalgamated zinc and hydrochloric have proven unsuccessful. The first experiment according to the iodine number showed signs of hydrogenation, but in all the others following no sign of reduction could be detected, so it must be assumed that the apparent reduction was due to some experimental error. Many modifications of the general method were tried, resulting in no reduction such as the use of the powdered zinc in place of granulated zinc, the substitution of iron filings for zinc; the addition of freshly amalgamated zinc from time to time throughout the run; the addition of acid in small amounts at regular intervals to keep up a vigorous evolution of hydrogen; the use of concentrated acid instead of dilute acid; the addition of copper sulphate to increase the evolution of hydrogen gas and the use of live steam to heat and thoroughly mix the three constituents, instead of the gas burner.

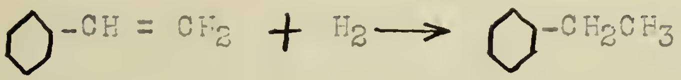
In every case saponification resulted with the formation

of free fatty acids which caused the treated oil to become more viscous than initially, and at times a solid at room temperature(24°). The longer the boiling was continued and the higher the temperature employed the greater the percentage of free fatty acids. The use of concentrated acid and also the addition of copper sulphate caused greater saponification, and without exception the greater the saponification the more solid was the oil at room temperature.

It is interesting to remember that when Clemmensen reduced acetophenone with amalgamated zinc and HCl he obtained ethyl benzene with no reduction of the unsaturation of the phenyl group. However, when Sabatier and Senderen's method of catalytic reduction was applied to acetophenone not only the carbonyl group but also the phenyl group is reduced which would demonstrate that the reducing power of amalgamated zinc and hydrochloric acid is less than that of catalytic nickel.

In view of the experiments this investigation, it would seem that the amalgamated zinc will not reduce an unsaturated hydrocarbon as Clemmensen claims, since he postulates the mechanism of reduction of acetophenone as follows:-





Part IV.

Electrolytic Reduction.

Electrolytic Reduction.

Part 1V.

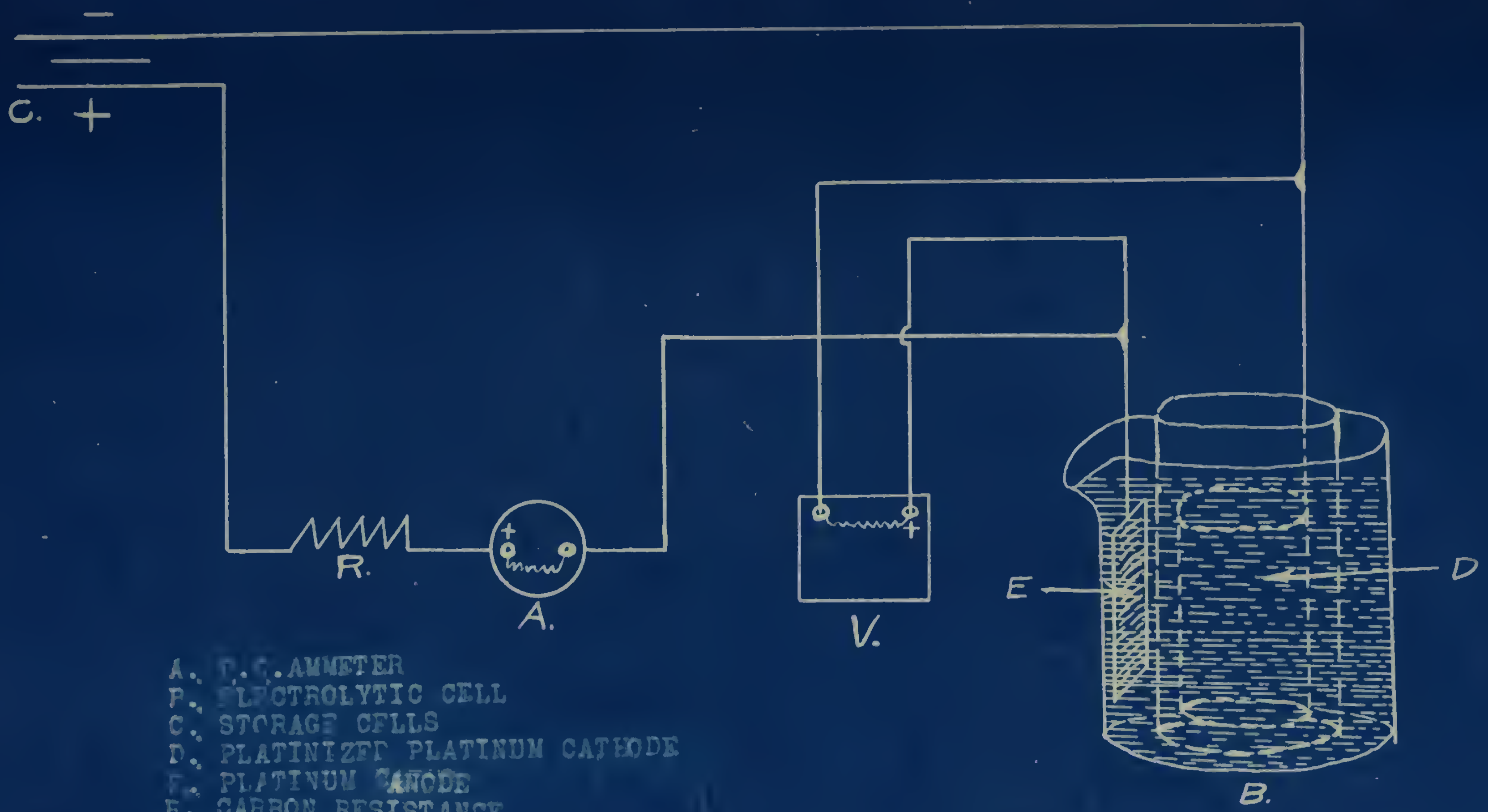
Two possibilities must be distinguished in the electrolysis of organic substances. The organic compound is either an electrolyte, i.e., a salt, base or acid or it is a non electrolyte. Since fatty acids and their glycerides are non electrolytes and do not conduct the current, other ions must be present for accomplishing the electrolysis. For this purpose, an inorganic acid as sulphuric or hydrochloric, is used. Then, primarily, the passage of the current does not at all affect this organic non-electrolyte. Only the ions are driven to the electrodes where they discharge themselves. At the instant, however, when the discharge occurs, the role of the organic substance begins. If it cannot react with the discharged ions, it is not affected by th the electrolysis; if it does react, it becomes a depolarizer. In an electrolytic cell, the cathode is capable of exerting a reducing action by the discharging of hydrogen ions, and the anode of exerting an oxidizing action. Obviously, when reduction alone is desired, the cathode and anode sections must be separated.

1. The Electrolytic Cell.

This cell was made as simple as possible, and consisted of a glass cylinder and a porous earthenware cup to serve as a diaphram, allowing passage of the current, but separating the anode and cathode. The porous cup contained the cathode.

2. Preparation of Electrodes.

The zinc electrodes were amalgamated by allowing the



A. D.C. AMMETER
B. ELECTROLYTIC CELL
C. STORAGE CELLS
D. PLATINIZED PLATINUM CATHODE
E. PLATINUM ANODE
R. CARBON RESISTANCE
V. D.C. VOLTMETER

zinc elcetrode to remain in a five percent solution of mercuric chloride for one hour. In all cells a platinum anode was used. The platinized platinum electrodes were prepared as follows:-[37]

The electrodes were thoroughly cleaned before hand with a strong solution of NaOH, then rinsed with distilled water several times and not touched again before platinizing. To insure a suitable kind of a black velvety coating on the electrodes the platinizing solution suggested by Lummer and Kurlbaum was employed. This was a 3% solution of commercial platinum chloride (H_2PtCl_6) to which was added 0.025% of lead acetate. Suitable current was obtained from two lead storage cells by introducing a carbon resistance until the evolution of hydrogen was moderate.

3. Arrangement of Apparatus for the Electrolytic Reduction.

The exact set up of the apparatus may be seen by the diagram on the opposite page. The typical arrangement for electrical decomposition is used, in which the current passes through an ammeter into the cell, and the terminals of a voltmeter are connected to the two electrodes. A carbon resistance is used to regulate the voltage and current density.

4. Materials Used.

1. Refined cottonseed oil used in the manufacture of soap.
11. Oleic acid. (Merck)
111. Fatty acids.

The method for preparing the fatty acid from the cottonseed oil and corn oil was as follows:-[38]

Fifty grams of the commercial oil are saponified by

by boiling with 40 cc of caustic potash solution (sp.gr. 1.4) and 40 cc of ethyl alcohol(95%) in a porcelain dish on a water bath till the soap becomes pasty. It is tested for total saponification by trying its solubility in ethyl alcohol. If there is any neutral fat, there will be an insoluble residue. The soap is dissolved in a liter of water and the soap solution is then decomposed by means of dilute sulphuric acid. When by continued boiling the fatty acids have been obtained as a clear oily layer free from solid particles floating on the aqueous liquid, the latter is drawn off by means of a siphon and the fatty acids are washed several times with hot water until the mineral acid has been removed. On standing over a water bath, the last traces of water and impurities will settle out leaving the fatty acids pure.

Experiment 1.

With the work of Bohringer and Sohne in mind, an attempt was made to hydrogenate oleic acid with a platinized platinum cathode in the above mentioned apparatus for electrolytic reduction.

Cathode.

Platinized sheet platinum 3 cm. by 3.6 cm was used making a total cathode surface of 21.6 sq.cm.

Anode.

Sheet platinum anode 3 cm. by 3.2 cm.

Cathode Solution.

Fifteen grams of oleic acid in 125 cc of ethyl alcohol(95%) with 8 cc of 20% H_2SO_4.

Anode solution.

Enough 20% sulphuric acid was used in the anode section to make anode and cathode solution of equal height or level.

Voltage.

The voltage was maintained constant between 4 and 6 volts.

Amperes.

The amperage was maintained constant between 0.01 and 0.15 amperes.

The current for the electrolysis was obtained from storage batteries. In this experiment as well as in all others to follow the line current and voltage across the two electrodes are maintained within certain limits as stated above. As soon as the electrolysis began an immediate evolution of gas was noticed at the anode, but no sign of evolution of a gas at the cathode. This would suggest that reduction of the oleic acid was taking place at the cathode. After about an hour a very slight evolution of gas began at the cathode and slowly became more pronounced. On stirring the cathode liquid, the evolution of gas would stop for a short time suggesting that some agitation was necessary to obtain efficient depolarization. It was found necessary to adopt a uniform method of sampling the cathode solution which at all times was as follows:-

The cathode solution is stirred vigorously to insure a uniform sample, and ten cc is pipetted off. On diluting with water the oleic acid or oil is thrown out of solution. By extraction with ether, washing free from mineral acid with distilled water, drying with anhydrous sodium sulphate, and distilling off

the ether, a pure sample is obtained.

After the electrolysis had continued two hours a sample was obtained, which although almost like the original oleic acid had a few solid crystals which suggested that stearic acid was slowly forming. The process was continued over night. Owing to the evaporation of the alcohol, it was necessary to add from time to time a little alcohol to keep the volume constant. The next morning the voltage had risen to 9 volts and a very vigorous evolution of gas at the cathode as well as anode was noticed.

After 38 hours of electrolysis, a sample designated (1) was taken and had the appearance of a light colored salve, which since the original oleic acid was a liquid under similar conditions, showed marked reduction. Twelve hours later another sample (2) was taken which was more solid than the previos one being of a lard like consistency at room temperature(24°). As stated above, the voltage was supposed to be maintained constant between 4 and 6 volts, but frequently it would vary, because there were several using the storage batteries at the same time. Hence, the results may be misleading due to the variation of conditions. The electrolysis was allowed to continue for twelve hours longer and sample (3) was taken which appeared even more solid than sample (2). The samples taken were too small to allow the determination of the titer, so the degree of reduction was traced by the iodine number.

Table X

Sample	Time hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3^*$	Iodine No.
Blank	-	-	53.8	-	-

Table X(con't)

Sample	Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$ *	Iodine Number
Blank	-	-	54.2	-	-
Original Oleic acid	-	0.2144	39.4	14.6	88.5
Original oleic acid	-	0.2970	34	20	87.6
Sample 1	38	0.2240	41.05	12.95	75.1
" 1	38	0.3635	32.4	21.6	77.2
" 11	50	0.2540	41.2	12.8	65.5
" 11	50	0.2705	40.0	14.0	67.3
" 111	62	0.3370	41.6	12.4	47.8
" 111	62	0.2340	45.3	8.7	48.3

* $Na_2S_2O_3$ equivalent to the iodine absorbed. 1 cc $Na_2S_2O_3$ is equivalent to 0.013 gram of iodine.

This experiment proves that with platinized platinum cathode,oleic acid can be reduced. Because of varying conditions this experiment shows little with regard to the efficiency of reduction or the possibilities of this process.

Experiment 11.

Since a zinc electrode should be one of the best cathodes for reduction according to the overvoltage theory, an attempt was made to reduce oleic acid after the same manner as in experiment 1. With the exception of using a zinc cathode 6 cm by 12 cm instead of the platinized platinum the conditions and solutions were kept the same as recorded in experiment 1.

Experiment 1 under 11.

Quite different from the previous experiment, a very vigorous evolution of gas, at both the anode and cathode began as

10¢ – 12 sheets.

soon as electrolysis was started. This would suggest that little reduction if any was taking place. After seven hours, a sample was taken which showed no signs of reduction; that is, no crystals appeared to form and it showed no tendency to solidify on slight cooling as did the sample in the previous experiment. The electrolysis was continued over night, and sampled again the next morning. Still the oil showed no sign of reduction. As before it was necessary to add alcohol from time to time to make up for the evaporation. The voltage(4-6) and the average amperage (0.1 -o.2) was maintained constant throughout the experiment and as at the beginning a vigorous evolution of gas from both anode and cathode continued. After the electrolysis had been going for 68 hours a sample was taken which even then showed no sign of reduction. It was concluded that no reduction has occurred, and the iodine number was not determined, since no reduction of the oleic acid could take place without some evidence of it in the way of greater viscosity, and tendency to solidify at ordinary temperatures.

Experiment 111.

The overvoltage of hydrogen from mercury electrode is greater than from a zinc electrode. Although no reduction was obtained with zinc cathode, according to the overvoltage theory, reduction might be expected from an amalgamated zinc electrode.

With this one exception, an amalgamated zinc cathode substituted for a platinized platinum cathode, the conditions and solutions were the same as recorded in experiment 1.

As in experiment 11 a vigorous evolution of gas

at the anode and cathode began simultaneously with the electrolysis. The electrolysis was continued over night and after eighteen hours a sample was obtained which showed no sign of reduction. The electrolysis was continued for 24 hours longer and the vigorous evolution of gas at the anode and cathode was constant throughout that time. A sample was taken which still showed no sign of reduction. After a total of 73 hours, electrolysis was stopped and a sample taken which even now showed no trace of reduction.

It was concluded that the vigorous evolution of gas at the cathode is a sign that little reduction if any occurs; that is the fatty acids are not acting in their capacity of a depolarizer.

Experiment 1V.

In order to determine whether the platinum black is the essential factor of the platinized platinum cathode, experiment 1 was repeated under similar conditions, with the exception that a platinum cathode, electrode surface 21.8 sq. cm., was substituted for the platinized platinum electrode.

As soon as the electrolysis was started a most vigorous evolution of gas began at both the anode and the cathode. The gas at the cathode seemed to just bubble up through the solution and out into the air which was not a good sign for effective reduction. After 8 hours a sample (1) was obtained which showed no sign of reduction and appeared the same as the initial oil. The gas was steadily evolved at the cathode as well as the anode suggesting the possibility of little reduction if any. A second sample(2) was taken after a total of 27 hours, but as before, no sign of

reduction. The electrolysis was continued for 16 hours longer and a sample taken which even then showed no sign of reduction so the electrolysis was stopped. It must be concluded that the platinum black is the essential factor in the successful reduction with the platinized platinum cathode.

Experiment V.

In order to make sure that experiment 1 could be repeated, this experiment was conducted using the same apparatus and materials indicated in Experiment 1.

As before when the electrolysis was started a vigorous evolution of gas was observed at the anode, but none at the cathode. About one half hour **after** it started, gas began to pass off from the cathode and as time went on the gasing at the cathode became more pronounced. The first sample (1) was taken after the electrolysis has run 22 hours and was of a lard like consistency at room temperature. It was noticed that the room temperature was lower than in the previous experiment. After 31 hours a crust of a white almost solid substance was formed over the upper layer of the cathode section and the cathode was greasy to the touch. This was presumably due to the evaporation of alcohol and the lower room temperature or possibly due to the stearic acid crystallizing out of solution. This layer of solid material was filtered off, sample (2) taken and the remainder returned to the solution. Alcohol, of course, was added to replace that removed or lost by evaporation. At this same time a sample (3) from the entire cathode section was taken. It was of

good color and the consistency of lard like sample(1) but apparently no harder, that is, no further reduced. The electrolysis was left to continue over night but the next morning the current was found turned off for some unknown reason so a sample (4) was taken and experiment discontinued. At the bottom of the cathode compartment, some of the finely divided platinum black had settled showing that the platinum black is not very adhesive and care must be taken to avoid a loss of platinum in this way. The degree of reduction as before was traced by the iodine number.

Table X1

Sample	Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$ *	Iodine Number
Blank	-	-	58.1	-	-
			58.5		
Blank	-	-	58.9	-	-
Initial	-	0.2334	41.9	16.6	87.5
Initial	-	0.2326	41.75	16.75	88.5
Sample 1	22	0.1692	49.3	9.2	66.8
" 1	22	0.2118	47.5	11.00	64.0
" 11	31	0.2090	46.95	11.55	68.0
" 11	31	0.2680	43.23	15.27	70.0
" 111	31	0.1850	47.80	10.7	71.0
" 111	31	0.1780	48.10	10.4	71.8
" 1V	31 plus	0.2504	45.25	13.25	65.0
" 1V	31 "	0.2595	44.95	13.55	64.3

* $Na_2S_2O_3$ equivalent to the absorbed iodine. 1 cc of $Na_2S_2O_3$ is equivalent to 0.0123 gram of iodine.

The iodine number of the various samples together with

the observations of conditions at different times show that the process of reduction or hardening proceeds rapidly until the gassing at the cathode becomes marked. Then too, since the iodine number of sample (2) the substance which separated out of the solution was practically the same as that of sample (3), a sample of t the entire cathode liquid at that time, the substance that separates out of solution must be a homogeneous mixture of the substanc in solution, and no more insoluble substance as stearic acid. It is further noted that there appears to be greater reduction after 22 hours than 31 hours. This might suggest dehydrogenation, but more probably is an experimental error. The platinum black evidently is not a very adhesive coating, and as such, great care and caution must be used to avoid losing it. At any rate, the results of experiment (1) were confirmed, and that was the purpose of this experiment.

Experiment VI.

In order to determine whether the reducing action is independent of the solvent used, acetone was substituted for ethyl alcohol.

Cathode.

Freshly platinized platinum, 3 cm long by 3.6 cm making a total cathode of 21.6 sq. cm was used.

Anode.

Of sheet platinum 3 cm, by 3.2 cm.

Cathode solution.

Fifteen grams of oleic acid was dissolved in 125 cc of aceto with 8 cc of 20% sulphuric acid.

Anode solution.

Enough of 20% H_2SO_4 was used to make the anode and cathode solutions the same level.

Volts.

The voltage was maintained constant between 5-6 volts.

Amperes.

The amperage was maintained constant between 0.10 ampere and 0.15 ampere.

As in the previous experiments as soon as the electrolysis started a vigorous evolution of gas began at the anode, but none at the cathode. After about one hour a slight gas evolution could be noticed at the cathode and as time went on it became more pronounced. The acetone evaporated more quickly than the ethyl alcohol and there was a greater tendency for the oleic acid to separate out of the solution, and consequently more frequent additions of solvent were needed. The first sample (1) was taken after the electrolysis had run 25 hours and was as light colored as the original oleic acid but almost solid at room temperature. At the time this sample was taken a very brisk evolution of gas was noticed at the cathode. However, the electrolysis was continued in order to determine whether efficient reduction occurred when the gas was evolved rapidly at the cathode. The second sample(2) was taken 23 hours later, but did not appear to be more solid than the first one. The initial volume of the solution was kept constant by frequent additions of acetone. After a total of 78 hours a third sample(3) was obtained. The iodine numbers were as follows:-

Table X11

Sample	Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$*	Iodine Number
Blank	-	-	58.5	-	-
			58.4		
Blank	-	-	58.3	-	-
Original Oleic acid	0	0.2520	40.4	18.0	87.8
Sample 1	25	0.2280	43.6	14.8	79.8
" 1	25	0.2590	42.0	16.4	78.0
" 11	47	0.2180	45.6	12.8	72.2
" 11	47	0.2056	46.0	12.4	74.2
" 111	78	0.2170	45.5	12.9	73.2
" 111	78	0.1970	46.5	11.9	74.3

* $Na2S_2O_3$ equivalent to the iodine absorbed. 1 cc of $Na_2S_2O_3$ is equivalent to 0.0123 gram of iodine.

These results would seem to indicate that equilibria was reached, and that in the acetone solution the reduction could not be carried beyond a certain point. But this could also be explained, in that, after the first twenty five hours gas was rapidly given off at the cathode, and since it was molecular hydrogen little reduction should be expected. Also because of the more rapid evaporation of the acetone the tendency of the oleic acid to separate out of the solution may have reduced the efficiency of the electrolysis.

Experiment V11.

Although cottonseed oil is not soluble in ethyl alcohol it is soluble in acetone, so an attempt was made to reduce the glyceride instead of the fatty acid.

Cathode.

The same cathode, 3 cm by 3.6 cm, a total surface of 21.6 sq. cm., was freshly platinized.

Anode.

The same anode of sheet platinum 3 cm by 3.2 cm.

Cathode solution.

Thirteen grams of cottonseed oil was dissolved in 160 cc of acetone with 7 cc of 20% H_2SO_4.

Anode solution.

Enough of the 20% sulphuric acid was used in the anode section to make it the same level as the solution in the cathode section.

Volts.

Three to five volts were maintained throughout the experiment.

Amperes.

The amperage was kept constant between 0.1 and 0.2 ampere.

As soon as the electrolysis was started a vigorous evolution of gas began at the anode and a slight evolution was noticed at the cathode. This gasing at the cathode gradually increased as time went on. After 16 hours sample(1) was taken and appeared to be the same as the original oil; that is, there was no sign of reduction. The cottonseed oil was found separating out of the solution at various intervals and frequent additions of acetone were needed to keep it in solution. A very small amount of water or acid caused the oil to separate out, and since the diaphragm allows the passing of water, it is evidently the cause

of the separation.

Sample (2) was taken after the electrolysis had been continued for 41 hours, but again there was no sign of reduction and the experiment was stopped at this point.

Apparently, the glyceride is more difficult to reduce than the fatty acid. Since, when any reduction has taken place, it is immediately noticeable by the greater viscosity or tendency to solidify, and no such sign of reduction was evidenced by the treated cottonseed oil, the iodine numbers were not determined.

Experiment V111.

Believing that with a larger electrode surface in the same volume of depolarizing solution as has been used, the reduction would proceed faster, and at the same time show the effect of varying conditions, two larger electrodes were obtained. The two were in the shape of hollow cylinders, and of the same size.

According to the observations made heretofore, agitation of the depolarizer would increase the efficiency or speed of the reduction and with this in view, this experiment was carried out.

Cathode.

One of the cylindrical sheet platinum electrodes 3.1 cm in diameter and 5.72 cm in depth was platinized(see comment below) in the usual way, making the total electrode surface 112 sq. cm.

Anode.

Of sheet platinum 4 cm by 3.4 cm.

Cathode liquid.

Fifteen grams of oleic acid dissolved in 130 cc of ethyl

alcohol(95%) with 7 cc of 20% H_2SO_4 was used.

Anode liquid.

Enough 20% H_2SO_4 solution was used to make the anode and cathode solutions of the same level.

Volts.

The voltage was maintained constant between 3-5 volts.

Amperes.

The amperage was maintained constant between 0.1-0.2 ampere.

When it came to platinizing this electrode, it was noticed that a grayish deposit was not obtained instead of the usual black velvety deposit. Even by varying the current density and voltage, the black deposit was obtained, but since the gray one appeared to be firm and uniform, it was decided to go ahead with the experiment.

In order to obtain agitation, a water motor connected to a screw shaped stirrer was used which slowly churned the cathode liquid. The electrolysis was started with the current obtained, as usual, from storage cells and a vigorous evolution of gas began at the anode. Although the cathode did not gas at the start, it began to evolve shortly after the beginning of the process. The stirrer seemed to be working alright but about an hour later the oleic acid had separated out of solution to the top of the liquid. The cathode solution was removed, alcohol added, and the oleic acid was placed in solution again, and the solution returned to the cathode compartment. After another hour the oleic acid was again out of solution, but since Bohringer and Sohne

claimed successful reduction of an emulsion of the fatty acid, the experiment was continued. After 1½ hours a sample(1) was taken which showed no sign of reduction. By this time there was a vigorous evolution of gas at both the anode and cathode.

At the end of 26 hours a sample (2) was taken which showed just a trace of reduction. The electrolysis was continued 24 hours longer, and then a sample(3) was obtained which appeared to be no further reduced than sample (2), so that the experiment was stopped at this point. Since there was little reduction, if any, the iodine numbers were not determined. Evidently this platinum black or gray coating is not as active as the preceding deposits on the cathodes. Also the stirring does not appear to be practical because it seems to throw the fatty acid out of the solution, and one of the essentials of this method is the solution of the depolarizer around the cathode.

Experiment 1X.

Along with the last experiment was carried out a similar one, with the other electrode mentioned above, but with one exception, cottonseed oil was substituted for the oleic acid. As before a grayish deposit of platinum was obtained. Another water motor with a screw stirrer connected with it was used, and since cottonseed oil is insoluble in alcohol, the best that could be expected was an emulsion of the alcohol, acid and cottonseed oil.

As soon as the electrolysis was started a vigorous evolution of gas began at the anode, and also slight gasing was noticed at the cathode which is not an encouraging observation in these experiments. After five hours a sample was taken which show-

ed no sign of reduction. As time went on, the gasing at the cathode increased. The stirrer did not keep the oil entirely emulsified for occasionally it was noted that the cottonseed oil separated out and to the top of the cathode liquid. Even after 72 hours there was no sign of reduction and the experiment was stopped. It was concluded that this grayish deposit of platinum was not nearly as active as the black velvety deposit and that less vigorous agitation of the solution would lessen the tendency of the fatty acid or cottonseed oil to separate out of the solution or emulsion as the case might be. Of course, this apparent lack of reduction might be due to the fact that the fatty acid or glyceride was not always in solution, but it was in solution long enough for a good amount of reduction if the electrode surface had been as effective a catalyser as in some of the previous experiments.

Experiment X.

From the results of the last experiments, it seems that the gray deposit of platinum does not give as good results as previous experiments where the deposit was black. Variation of current density or voltage did not give the desired black deposit. After several trials in varying the concentration of the platinum chloride solution and the distance of the electrodes from the cathode during the deposition of the platinum it was found that the closer the anode to the cathode the darker and heavier the deposit of platinum; and further more, the more dilute solution of the platinum chloride(2%) favored the darker deposit. Hereafter, the dark velvety deposit of platinum was readily obtained by observing the above mentioned conditions; namely, a dilute solution of

platinichloride and close proximity of the anode and cathode during the deposition of the platinum.

Experiment XI.

As yet the oleic acid has not been totally reduced, and in order to demonstrate that the iodine value can be reduced nearly to that of pure stearic acid by this method experiment 1 was repeated.

Cathode.

The cylindrical platinum cathode 3.1 cm in diameter and 5.72 cm in depth was platinized in the usual way and this time a black velvety deposit of the platinum was obtained as described in the previous experiment.

Anode.

Of sheet platinum 3 cm by 3.2 cm.

Cathode liquid.

Fifteen grams of the oleic acid were dissolved in 130 cc of ethyl alcohol(95%) with 7 cc of 20% sulphuric acid.

Anode liquid.

Enough 20% sulphuric acid was used to make the anode and cathode solutions of the same level.

Volts.

A constant voltage between 4 and 5 volts was maintained.

Amperes.

A constant amperage between 0.1 and 0.25 ampere was maintained.

The electrolysis was started and as usual a vigorous evolution began at the anode and none at the cathode. But after

about an hour a slight gas evolution could be detected at the cathode which as time went on became more pronounced. Alcohol was added accasionally to keep the initial volume. After twelve hours a white solid began to separate out of the solution, but only in small quantities. This white solid carried down with it some of the very finely divided platinum black which could be seen through the clear solution. This was later filtered off and the platinum so recovered. At the end of 28 hours a sample was taken which seemed even more solid than ordinary tallow at room temperature. By this time the gasing at the cathode was very brisk. In order to determine whether the white solid separating out was further reduced than that in solution sample (2) was taken which was just like paraffin at room temperature, and could be readily chipped with a knife. It was almost pure white. The electrolysis was continued for 76 hours, sample (3) was taken and the electrolysis stopped. The cathode was covered with the white solid which separated out, and at the end of this experiment the hydrogen was freely evolved. Throughout the experiment there was a tendency for the voltage to rise, but it was regulated by the carbon resistance. Of course in lowering the voltage the current was lowered also. The iodine numbers were determined with the results as follows:-

Table XIII

Sample	Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$*	Iodine Number
Blank	-	-	57.6	-	-
Original	-	0.2156	42.2	15.40	89.4
Sample 1	28	0.1988	56.25	1.35	8.5
" 1	28	0.2320	55.90	1.70	9.1

Table X111(con't)

Blank	Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$*	Iodine Number
Sample 11	28	0.2024	57.0	0.60	3.7
" 11	28	0.2296	56.85	0.75	4.0
" 111	76	0.2605	56.75	0.85	4.1
" 111	76	0.3175	56.25	1.35	5.3

* $Na_2S_2O_3$ equivalent to the iodine absorbed. 1 cc of $Na_2S_2O_3$ is equivalent to 0.0125 gramof iodine.

The original oleic acid was liquid at room temperature but the treated oleic acid sample 111 had a titer of 39°.

The experiment demonstrates that 94% of the oleic acid was completely reduced to stearic acid. Moreover the black velvety deposit of platinum obtained in experiment 9 gives good results and shows without doubt that the nature of the deposit of platinum has much to do with the effectiveness of the reduction.

Experiment X11

Since this method of reduction is successful with one of the fatty acids, oleic acid, it will now be tried with mixed fatty acids obtained from cottonseed oil.

Cathode.

The cylindrical platinum cathode 3.1 cm in diameter and 5.72 cm in depth used in the last experiment was replatanized in the usual way and a velvety black deposit obtained.

Anode.

Of sheet platinum 3 cm by 3.2 cm.

Cathode liquid.

Fifteen grams of the cottonseed oil fatty acids were

dissolved in 130 cc of ethyl alcohol(95%) with 7 cc of 20% sulphuric acid.

Anode liquid.

As before, enough of the 20% sulphuric acid was used to make the anode and cathode liquids of the same level.

Volts.

The voltage was kept constant between 4 and 6 volts.

Amperes.

A constant amperage between 0.15 and 0.25 ampere was maintained.

As usual when the electrolysis started the anode gases freely and the cathode not at all, but gradually the gasing becomes more and more noticeable. The fatty acids stayed in solution, but there appeared to be a coating of white solid forming on the cathode. The lack of a vigorous gas evolution at the cathode while the anode gases freely is a good sign that reduction is taking place, because were not the fatty acids acting as a depolarizer, the gas would be readily given off at the cathode from the beginning. Sample (1) was taken after the electrolysis had been going for 31 hours. There was an accident and this experiment was discontinued. The iodine numbers were determined with the following results:-

Table XIV

Sample	Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$*	Iodine Number
Blank	-	-	57.6	-	-
Original cottonseed oil fatty acids	0	0.2978	32.60	25.0	105.2

Table XlV(con't)

Sample	Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$*	Iodine number
Original cotton seed oil fatty acids	0	0.2768	34.15	23.45	106.1
Sample 1	31	0.2510	49.10	8.5	42.3
" 1	31	0.2835	47.90	9.7	43.0

* $Na_2S_2O_3$ equivalent to the iodine absorbed. 1 cc of $Na_2S_2O_3$ is equivalent to 0.0125 gram of iodine.

Experiment Xlll.

In order to determine the conditions under which the reduction proceeds most rapidly, and to trace the process of reductionwith this method by the decrease of iodine value with time, this experiment was carried out.

Cathode.

The cylindrical cathode 3.1 cm in diameter, and 5.72 cm in depth was coated with a uniform black velvety deposit of platinum.

Anode.

A sheet platinum anode 3 cm by 3.2 cm was used.

Cathode liquid.

Fifteen grams of oleic acid was dissolved in 130 cc of ethyl alcohol(95%) with 8 cc of 20% sulphuric acid.

Anode liquid.

Enough of the 20% sulphuric acid solution was used to make the anode and cathode solution the same level.

Volts.

The voltage was maintained constant between 2.5 and 5 volts.

Amperes.

The amperage was maintained constant between 0.15 and 0.25 ampere.

As heretofore, the current for the electrolysis was obtained from storage cells. As usual, a vigorous evolution of gas began at the anode when the electrolysis started, but none was evolved at the cathode, suggesting that the hydrogen was being absorbed at the cathode. After about two hours the cathode began to evolve gas slightly, and as time went on the gasing became more pronounced. In order to maintain the same conditions and quantities of materials throughout the experiment very small samples were taken. After 6.5 hours sample (1) was obtained which appeared to be almost solid at room temperature(25°). From this time on a vigorous evolution of gas continued at the cathode, and the cathode gradually became coated with a white layer of the reduced oleic acid. As time went on little particles of this white solid would settle to the bottom of the cathode compartment. Sample(2) was taken ten hours later and appeared to be even more solid than the previous sample. It was necessary to add alcohol from time to time to maintain the iniatial concentration. Eight hours later sample (3) was taken, but for some unknown reason turned to a dark brown color and was discarded. After a total of 30.5 hours sample (4) was taken which did not appear to be quite as solid as the previous sample. The gasing at the cathode had increased and at

this time was gasing freely. Eleven hours later sample(5) was obtained which appeared more solid than any previous sample of this experiment. After a total of 50.5 hours a sample(6) was taken which seemed about the same as the previous one. For the past thirty hours there had been a vigorous evolution of gas at the cathode, and the cathode was still covered with the white solid, so after a total of 64.5 hours a sample (7) was taken and the experiment stopped. The samples previous to this last one were too small to enable the titer determination, but the titer of the last sample,(titer 46.5°) the hydrogenated oleic acid was much higher than the unhydrogenated oleic acid which was a liquid at room temperature(25°). The iodine values were determined and the results were as follows:-

Table XV

Sample	Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$*	Iodine Number
Blank	-	-	58.5	-	-
Initial acid	-	0.2520	40.5	18.00	87.8
Sample 1	6.5	0.1386	52.85	5.65	50.2
" 11	16.5	0.2328	51.05	7.45	39.5
" 1V	30.5	0.2457	49.85	8.45	43.3
" V	41.5	0.1987	54.30	4.20	26.0
" V1	50.5	0.2468	52.35	6.15	30.7
" V11	64.5	0.2724	54.25	4.25	19.1

* $Na_2S_2O_3$ equivalent to the iodine absorbed. 1 cc of $Na_2S_2O_3$ is equivalent to 0.0123 gram of iodine.

This experiment clearly demonstrates that evolution of

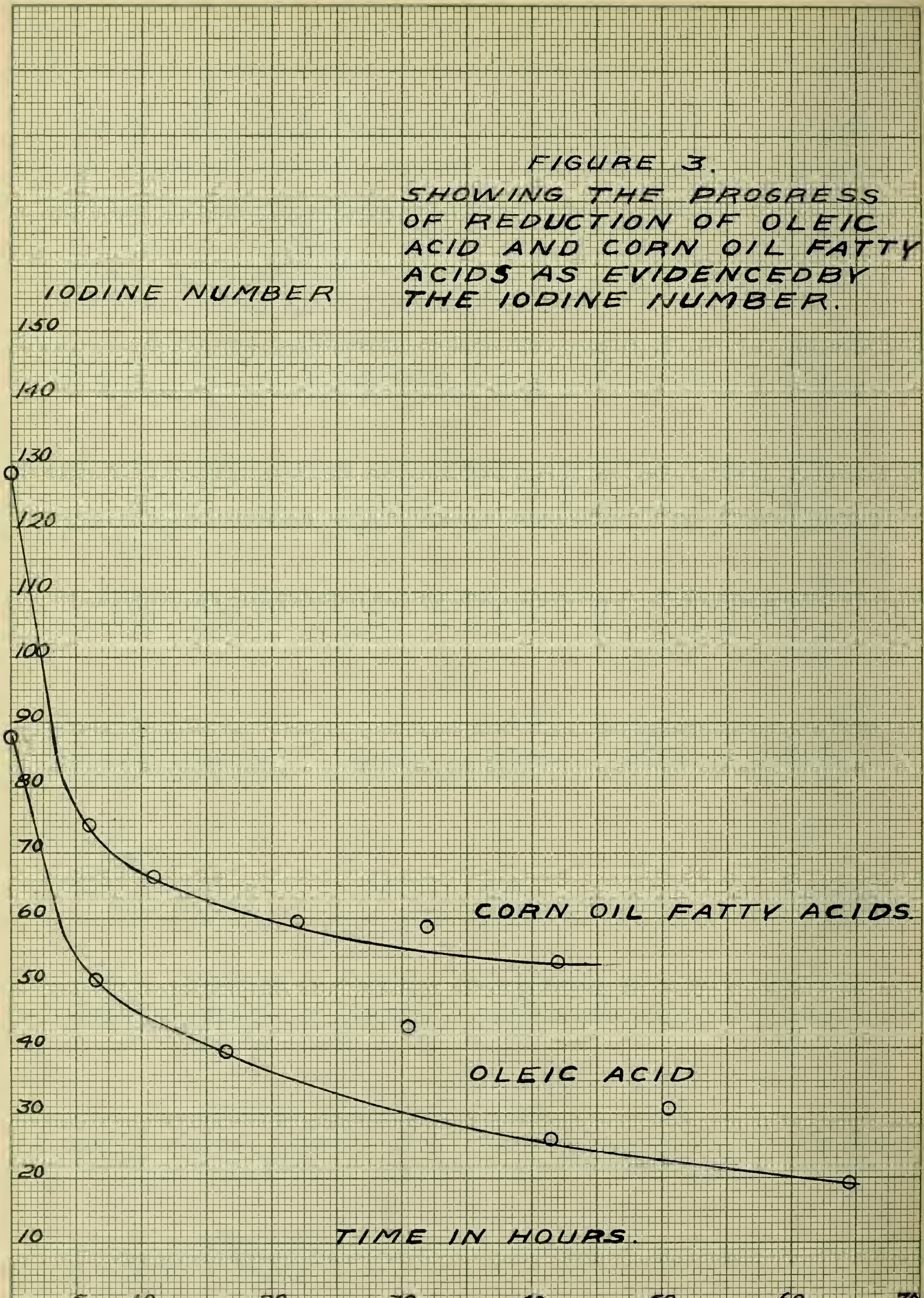


FIGURE 3.
SHOWING THE PROGRESS OF REDUCTION OF OLEIC ACID AND CORN OIL FATTY ACIDS AS EVIDENCED BY THE IODINE NUMBER.

gas at the cathode means loss of reduction, because during the first few hours or until evolution of gas at the cathode begins, the reduction proceeds rapidly and as the gasing becomes more pronounced the reduction proceeds more slowly. The apparent variation from the curve must have been due to the inability to secure uniform samples, because of the solid material which separated out of solution.

Fxperiment XlV .

This experiment was an exact repetition of the last one with the exception that corn oil fatty acids were used instead of oleic acid, and the purpose being to note whether the method was again successful with mixed fatty acids and also to observe whether the reduction proceeded in the same way; that is, whether the curve for the iodine value against time as found in the last experiment was typical of the reduction by this method and this apparatus or whether there could be an entirely different curve for different kinds or mixtures of fatty acids. The conditions, cathode, cathode liquid and etc., were the same as in the previous experiment, and the current for the electrolysis was obtained from storage cells.

As usual a vigorous evolution of gas began at the anode as soon as electrolysis started, but none at the cathode. Even after six hours there was no sign of the evolution of gas at the cathode which showed that a good amount of reduction must be taking place. At this time, after six hours, sample (1) was taken which was almost solid at room temperature(25°) whereas, the initial sample was a liquid at the same temperature. Six hours later,

just a slight evolution of gas at the cathode was noticed, and also that the cathode was being coated with a white solid. The voltage had risen slightly and the current dropped. At this time sample (2) was taken and the electrolysis allowed to continue over night. The next morning the voltage had risen to 7.5 volts and the current dropped to less than one tenth of an ampere. The cathode was gasing freely, and covered with a white coating of the reduced material. Apparently this white coating increased the resistance, increasing the voltage and decreasing the currnet density. To determine whether this was the cause for the higher voltage, the cathode was taken out of solution, the white solid removed by extraction with a mixed alcohol and ether solution, but it was noted that considerable platinum black came off by this treatment which again demonstrated how carefully this process must be watched to avoid losing platinum black. At this time sample(3) was taken and was a solid at room temperature (25°), total time of run to this point 22 hours. The electrolysis was continued and the white coating on the cathode was again noticed. From now on the cathode evolved gas freely. After a total of 32 hours sample (4) was taken which appeared to be the same as sample (3). The voltage rose gradually as the white coating became heavier. After a total run of 42 hours, the electrolysis was stopped and sample (5) taken which was a solid at room temperature. Titer of hydrogenated corn oil fatty acids 41.4°.

The iodine numbers were obtained with the results as follows. Small samples were taken, in order not to decrease the initial content, 15 grams, which accounts for only one iodine

number being determined for each.

Table XV1

Sample	Time Hours	Weight	$Na_2S_2O_3$	$Na_2S_2O_3$*	Iodine Number.
Blank	-	-	58.5	-	-
Initial fatty acid	0	0.1945	38.25	20.25	128.1
" "	0	0.1960	38.20	20.3	128.0
Sample 1	6	0.2133	45.65	12.85	74.2
" 11	12	0.1942	48.0	10.5	66.4
" 111	22	0.2290	47.4	11.1	59.6
" 1V	32	0.2263	47.7	10.8	58.7
" V	42	0.2563	47.4	11.1	53.2

* $Na_2S_2O_3$ equivalent to the iodine absorbed. 1 cc of $Na_2S_2O_3$ is equivalent to 0.0123 gram of iodine.

As in the previous experiment, the reduction proceeds very rapidly for the first six hours or until the gasing at the cathode becomes pronounced and then the reduction proceeds at a much slower rate, and after a short time is hardly reduced at all. This must be due to the formation of the white coating which prevents the fatty acid from acting as an efficient depolarizer. In order to obtain efficient reduction this coating must be avoided, This experiment bears out the previous view; namely, that evolution of gas at the cathode is a good indication of lack of reduction, or loss, since excellent efficiency is obtained before gasing commences. This could probably be effected by the proper agitation of the cathode liquid and should be studied from that viewpoint.

General Summary and Conclusion.

General Summary and Conclusion.

As has been stated, according to the overvoltage theory a zinc or mercury cathode should be the most efficient and a platinized platinum cathode the least efficient for electrolytic reduction. It has been found that no reduction of fatty acids or their glycerides take place at zinc or amalgamated zinc cathodes in the electrolytic cell, heretofore described, while with a platinized platinum electrode very efficient reduction was obtained. Although the best conditions for reduction at zinc or amalgamated zinc may not have been present, it would seem that at least a trace of reduction should have been detected.

As for the platinized platinum cathode, the effective reduction must be attributed to the occlusion of hydrogen by the platinum black, that is, to its well known activity as a catalyst for reduction, because a platinum cathode under similar conditions does not reduce the fatty acid or its glyceride. Hence this method must be looked upon as a combined electrolytic and catalytic method whereby the electrolysis furnishes the hydrogen at such a rate that in the presence of the platinum black, the fatty acids acting as depolarizers are reduced. This method was successfully applied in the reduction of oleic acid, cottonseed oil and corn oil fatty acids, and as high as 91% of the fatty acid has been reduced to stearic acid in 28 hours with an electrode surface of 112 sq. cm., using an average voltage of 4 volts and an average of 0.15 ampere.

Attempts were made to reduce the glycerides, which are not not soluble in ethyl alcohol, but without success, although

Boehringer and Sohn[19] claim that this method is successful when either the fatty acid or its glyceride is in solution or in an emulsion as the cathode liquid.

When the electrolysis starts no gas is evolved at the cathode and reducing proceeds very rapidly, but before long evolution of gas begins at the cathode, and as time goes on becomes more pronounced. At the same time the reduction slows up as seen by the curves in experiments 12 and 13. This phenomena is followed by the slow appearance of a white coating of the reduced material on the cathode, and obviously must be the cause of the lack of depolarization by the cathode liquid which accounts for the slowing up of the reducing process and evolution of gas at the cathode. In further study of this method, the problem would be to prevent the coating of the cathode and thereby maintaining the reducing conditions, existing at the beginning of the electrolysis, until the depolarizer was completely reduced.

Any deposit of finely divided platinum will not be as effective as another, because in this study, it was found that a gray deposit of platinum did not give nearly as good results as the black velvety deposit which was obtained by using dilute(2%) solution of platinum chloride and keeping the anode and cathode close together. This platinum black does not adhere very well to the platinum, for time and again some of this black would be found at the bottom of the cathode compartment. Aside from the possible loss of platinum the cost of maintaining the electrodes would be negligible, because no platinum is used up in the process. In addition this is a quick, clean and cheap method of reduction,

since when the conditions are right the reduction proceeds very rapidly; clean because there are no secondary products formed as in many strictly chemical reactions, and cheap, because the electrical power consumption is small.

However, in a problem of this kind, there are many variables to contend with, for example, voltage, current density, acid and acid concentration, solvent, nature and shape of the electrodes, temperature, and many others. After a study such as this, one begins to realize the enormous possibilities of electrolytic reduction when the individual effect of each variable has been worked out.

As a final conclusion, I wish to quote from Sidgwick[39] who expresses my views with regard to the possibilities of electrolytic reduction.

" We may consider that the electrolysis is a means of preparing on the surface of the cathode a solution of hydrogen, the concentration of which can be varied, as it depends on and is measured by the difference of potential between the cathode and the solution. It is only limited by the fact that at a certain concentration the hydrogen is given off at the cathode in bubbles; but even this limit can be altered by changing the material of the cathode. We are thus able, by using the electrolytic method, to obtain the same variation of results as would be produced chemically by reducing agents of greater or less strength, and this without the complications which are necessarily introduced in the chemical method by changing the nature of the substances present."
As yet, so little is known about reduction, or electrolytic organic chemistry that it offers a profitable field for advanced study.

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